Compositional Optimization of Polyimide-Based SEPPI Membranes Using a Genetic Algorithm and High-Throughput Techniques

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Asymmetric, nanosized zeolite-filled solvent resistant nanofiltration (SRNF) membranes, prepared from emulsified polyimide (PI) solutions via the earlier reported solidification of emulsified polymer solutions via phase inversion (SEPPI) method, were optimized for their performance in the separation of rose bengal (RB) from 2-propanol (IPA). All membranes were prepared and tested in a parallellized, miniaturized, and automated manner using laboratory-developed high-throughput experimentation techniques. Nine different synthesis parameters related to the composition of the casting solutions were thus optimized. In a first, "conventional" approach, a preliminary systematic screening was carried out, in which only four constituents were used, that is, Matrimid PI, NMP as solvent, THF as volatile cosolvent, and an NMP-based zeolite precursor sol as emulsifying agent. A combinatorial strategy, based on a genetic algorithm and a self-adaptive evolutionary strategy, was then applied to optimize the SRNF performance of PI-based SEPPI membranes. This directed approach allowed the screening of an extended, 9-dimensional parameter space, comprising two extra solvents, the two corresponding nanosized zeolite suspensions, as well as another cosolvent. Coupling with high-throughput techniques allowed the preparation of three generations of casting solutions, 176 compositions in total, resulting in 125 testable membranes. With IPA permeances up to 3.3 L.m^{-2} h^{-1} bar^{-1} and RB rejections around 98%, the combinatorially optimized membranes scored significantly better with respect to fluxes and selectivities than the best membranes obtained in the systematic screening. The best SEPPI membranes also showed much higher IPA permeances than two commercial SRNF membranes at similar or slightly lower RB rejections.

Introduction

Solidification of emulsified polymer solutions via phase inversion (SEPPI) has recently been presented as a novel approach to create porous polymeric structures with controlled porosity.[1] SEPPI involves the preparation of an emulsified polymer solution through the addition of an organic suspension containing nanosized silicalite-1 particles,[2] or surfactants. Subsequently, this polymeric emulsion is solidified by simple contact with a polymer nonsolvent, with the droplets forming a template for the final pores. A wide variety of polymers could thus be turned into porous materials with tunable pore characteristics via a number of easily accessible parameters at the level of the emulsion. Thanks to the nanodimensions of the particles and the insertion of an evaporation step prior to solidification of the cast films, highly selective asymmetric polyimide (PI) membranes with thin skin layers could be prepared for use in solvent resistant nanofiltration (SRNF).[3] With respect to their mechanical stability, organomineral SEPPI membranes[4] behaved superior to unfilled reference membranes and compared favorably with commercial SRNF membranes in terms of fluxes and selectivities. Optimization of the post-casting conditions and a special post-treatment allowed a significant performance improvement, as reported elsewhere.[5]

As a membrane process able to separate organic mixtures down to a molecular level, typically at pressures between 5 and 20 bar, SRNF has a huge potential in treating nonaqueous streams,[3,6] mainly found in the food,[7] petrochemical,[8] fine-chemical,[9] pharmaceutical,[10] and photochemical industries.[11] SRNF membranes are typically applied to retain organic compounds with molecular weights ranging from 200 to 1000 g mol^{-1}. Solvents permeating through SRNF membranes are easily recycled, while retained solutes can be effectively purified because of their significant increase in concentration. Environmental and economical concerns explain the steadily increasing interest in SRNF as a sustainable technique to treat solvent streams, offering a great advantage over traditional separation techniques, such as energy-intensive distillations, waste-generating extractions, and solvent-consuming chromatographical separations. Because of their chemical stability, Matrimid,[12] as well as other types of PIs[13] have been used to prepare integrally skinned asymmetric SRNF membranes,[3,14] and the PI-based Starmem membranes currently still represent the benchmark in SRNF.[3]

In view of the expected growth of the SRNF market, a clear need still exists to develop more and better membranes

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to solve separation problems in existing industrial processes and open new application areas. As many parameters are involved in membrane synthesis, for instance via phase inversion, membrane optimization has always been time-consuming. Using a traditional parameter-by-parameter approach, in which a restricted number of parameters is systematically, but independently screened, the development of a new membrane with optimal properties in the envisaged separation would be extremely slow, hence inefficient, but also ineffective since it is very improbable to find the overall optimum of such extended parameter space in this way.

An important challenge in developing and optimizing novel, robust, high-performance membranes is thus to find and implement more efficient search strategies, which rapidly focus on the most promising spots within the parameter space, thus increasing the chance on finding the membrane with the best separation of the targeted compounds. High-throughput (HT) experimentation and design of experiment (DoE) methods have been introduced to minimize the experimental efforts at maximal information output.[15] Originally developed for drug discovery applications,[16] and since then applied to an ever increasing number of materials, such as catalysts[17] and polymer-based materials,[15a,18] these techniques were recently introduced in membrane research with the successful combinatorial optimization of Matrimid-based asymmetric SRNF membranes.[19] This optimization was carried out in an 8-dimensional compositional parameter space, comprising PI, NMP, two volatile cosolvents, and four nonsolvent additives. A genetic algorithm (GA) was used to obtain a fast and straightforward optimization for the separation of the dye methyl orange from 2-propanol (IPA). The development of a laboratory-designed HT filtration cell that allows a rapid and accurate screening of large sets of membranes was an essential prerequisite for the successful implementation of the algorithm.[20] Not only the HT testing but also the complete membrane preparation was miniaturized and parallelized, using an automatic liquid handler and a film applicator.[19]

Similar to the principles of evolution and natural selection found in nature, GAs iteratively generate successive generations of materials by applying evolutionary operators, such as mutation and cross-over, in a fitness-proportional and self-adaptive manner, in such a way that the created populations undergo a steady evolution so as to quickly approach an optimal solution for the optimization problem.[21] Contrary to other DoE strategies, GAs allow the use of continuously variable parameters. They are furthermore not limited by the boundaries of the starting library and can thus escape local optima and enter new regions of the parameter space by themselves.[15a]

Considering the promising performance of Matrimid-based asymmetric SEPPI membranes in SRNF,[1,5] the present paper will focus on the compositional optimization of these membranes for the separation of rose bengal from IPA, using a similar HT/combinatorial approach as applied earlier for unfilled PI-membranes.[19] This study thus intends to confirm the strength of such directed search approach to optimize membrane compositions. The selected test solute is a dye with a molecular weight of 1017 g mol^{-1} for which a rejection >90% would imply that the membrane involved can be referred to as a SRNF membrane. First, a classical systematic screening will be carried out in a quaternary parameter space, comprising Matrimid, NMP as solvent, THF as volatile cosolvent, and an NMP-based nanosized zeolite sol as emulsifying additive, being the constituents originally used for the preparation of PI-based SEPPI membranes.[1,5] This preliminary screening will serve as reference for a subsequent combinatorial study, based on a GA and using HT synthesis and screening techniques, to further improve the performance of the membranes. Apart from the four parameters mentioned above, two extra solvents (DMSO and DMAc), the two corresponding nanosized zeolite suspensions, and an extra cosolvent (1,4-dioxane) will be used. The anticipated advantages of using a GA not only include the possibility to extend the parameter space from four to nine components but also the chance on finding the overall optimum of the space. The optimized SEPPI membranes will also be compared with the commercial SRNF membranes Starmem 120 and MPF-50.

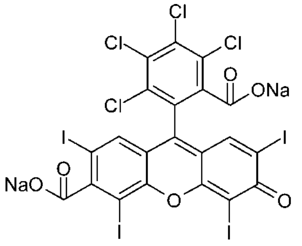


Figure 1. Molecular structure of RB.

Experimental Section

Materials. Polyimide (PI, Matrimid 9725 US) was kindly supplied by Huntsman (Switzerland) and dried overnight at 130 °C prior to use. *N*-Methylpyrrolidinone (NMP), dimethylsulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), tetrahydrofuran (THF), 1,4-dioxane (Diox), 2-propanol (IPA), toluene, and 2-methyl-4-pentanone (MIBK) were all purchased from Acros and were used without further purification. Rose bengal (RB, 1017 g/mol), shown in Figure 1, was obtained from Fluka, and the mineral oil P3 was purchased from Pfeiffer. A polypropylene/polyethylene (PP/PE) nonwoven backing (Viledon FO2471) was provided by Freudenberg (Germany). Commercial SRNF membranes Starmem 120 and MPF-50 were purchased from Membrane Extraction Technology (London, U.K.) and Koch Membrane Systems (Wilmington, MA), respectively.

Automated HT Preparation of Casting Solutions. Miniaturized PI solutions were prepared in 22 mL glass vials (Supelco) with PTFE/silicone septa by means of an automated liquid handler (Genesis RSP100, Tecan, Switzerland), equipped with 4 fixed tips provided with septum-piercing needles.[19] The robot was connected to a PC and operated by Gemini software in which a Microsoft Excel pipetting list was incorporated, thus guaranteeing full automation. Matrimid polymer was manually weighed in the flasks, after which the liquid constituents were added by the liquid handler in the order solvents > nanosized zeolite additives > cosolvents. Three different solvents (NMP, DMSO, and

DMAc), the three corresponding nanosized zeolite sols (NMP-S, DMSO-S and DMAc-S), and two volatile cosolvents (THF and Diox) were used. Similar to the synthesis of NMP-S, polymer-compatible DMSO-S and DMAc-S additives were generated from an aqueous silicalite-1 precursor suspension by a solvent exchange procedure.[1] The total weight of all casting solutions was set at 5 g. Polymer solutions, 16 at a time, were homogenized overnight using a HT mechanical stirrer (Agila, Belgium) at 1000 rpm.

Membrane Preparation. Integrally skinned asymmetric membranes were prepared via immersion−precipitation. Homogeneous PI solutions were cast four by four at room temperature on a PP/PE nonwoven fabric, fixed on a stainless steel plate, using an automatic film applicator (Braive Instruments, Belgium) at a speed of 1.2 m min^{-1}, and a custom-made casting box, compartmentalized in four 54 mm wide sections.[19] Subsequently, the cast films with a wet film thickness of 250 μm were exposed to ambient air for 30 s to allow partial evaporation of the solvents. The sheets with the nascent films were then immersed in deionized water at room temperature. Membranes were post-treated via solvent-exchange, involving immersion in IPA for 3 h, and subsequently for 3 days in a toluene/MIBK/mineral oil solution with a 40/40/20 volume ratio. Finally, the oil-impregnated membranes were vacuum-dried at 65 °C for 1 h.[12,19,20]

High-Throughput Membrane Testing. Room-temperature filtration experiments were performed on a laboratory-developed, dead-end 16-unit HT filtration module, which allowed simultaneous testing of 16 membranes at controlled pressures in mechanically stirred cells with an active filtration area of 4.52×10^{-4} m^2 each.[20] Circular coupons were cut from the membrane sheets, mounted in the bottom plate of the HT cell, and sealed with Viton O-rings. A 70 μmol L^{-1} RB solution in IPA was used as a typical SRNF feed. Feed solutions (0.030 L) were poured into the cells, stirred at 700 rpm, and subjected to 10 bar nitrogen pressure. Initial permeates collected during the first 15 min of filtration were discarded, after which samples were collected in cooled flasks for typically 15 min, weighed, and analyzed. Permeances (P) are expressed in L m^{-2} h^{-1} bar^{-1}, while rejection rates R (%) are defined as $(1 - C_p/C_f) \times 100$, in which C_f and C_p refer to the solute concentrations in the initial feed and in the permeates, respectively. Dye concentrations were recorded on a Perkin-Elmer Lambda 12 UV−vis spectrophotometer at 558 nm. Membranes were generally tested in duplicate and three times in case of a standard deviation of >10%. In graphs and tables, average performance values are shown.

Evaluation of Membrane Fitness. All prepared membranes, in the traditional screening, as well as in the combinatorial study, were evaluated for their performance in the RB/IPA separation. To be able to compare and rank the membranes, a fitness or objective function (OF) was defined, taking into account both permeance (P) and rejection (R) values. With a target performance (B), combining a RB rejection of 100% and an IPA permeance (P_{target}) of 6 L m^{-2} h^{-1} bar^{-1}, and a threshold retention ($R_{\text{threshold}}$) of 70% (A), the following operations allowed conversion of the measured permeance (P_{measured}) and rejection values (R_{measured}) of a particular membrane (C) to coordinates (C_1, C_2) ranging from 0 to 100.

$$C_1 = \frac{P_{\text{measured}}}{P_{\text{target}}} \times 100 \tag{1a}$$

$$C_2 = \frac{(R_{\text{measured}} - R_{\text{threshold}})}{(100 - R_{\text{threshold}})} \times 100 \tag{1b}$$

P_{target} and $R_{\text{threshold}}$ were chosen to adjust the weight of both performance components in OF. The value of OF was then calculated for each membrane by subtracting the distance BC ((C_1,C_2) − (100,100)) from the distance AB ((0,0) − (100,100)) in the coordinate space, using Pythagoras' law: the smaller the distance BC between the data point and the target point, the higher the OF value. Thermodynamically unstable casting solutions and solutions resulting in defective membranes with rejection values below $R_{\text{threshold}}$, were given a zero OF value.

Results and Discussion

Systematic Screening in a Ternary/Quaternary Parameter Space. Ternary Parameter Space. In first instance, casting solutions were prepared containing Matrimid, NMP, NMP-S, and THF, keeping the THF/NMP weight ratio constant at 0.33. The volatile THF, which was allowed to evaporate prior to solidification of the cast film, was added to create a dense skin layer.[3,14] The membrane screening was carried out for three distinct PI concentrations, that is, 14, 18, and 22 wt %, all within the earlier defined compositional boundaries for emulsified PI solutions.[1] For each of these PI concentrations, the NMP-S concentration was varied between 6 and 30 wt% with steps of 4 wt%. Membranes are represented as PI*x*/*y* with x and y denoting the PI and NMP-S concentration (wt%) of the casting solution involved, respectively. All membranes were tested with the HT module in the separation of RB from IPA at 10 bar and room temperature. No fouling was observed. The membranes in Table 1 are ordered according to their OF, calculated with a P_{target} value of 6 L m^{-2} h^{-1} bar^{-1} and a $R_{\text{threshold}}$ value of 70%. A high OF can clearly result from either a high P combined with a relatively low R (e.g., PI14/10) or a lower P combined with a high R (e.g., PI18/18). The screening results indicate a maximum OF for membranes cast from PI solutions containing 18 wt % polymer and relatively low amounts of NMP-S. Also the membranes originating from less concentrated PI solutions (14 wt%) with higher NMP-S content generally perform well. The majority of the prepared SEPPI membranes compares favorably with the best commercial SRNF membranes. The best membrane in Table 1 displays an OF value which almost doubles the one of the PI-based Starmem 120 membrane, corresponding to a 5-fold flux increase combined with a relatively small rejection decline. Compared to MPF-50, the permeance of the best SEPPI membrane is even 7.4 times higher, at the expense of an even smaller loss in selectivity. This significant improvement in overall performance compared to the industrial benchmark membranes clearly indicates the potential of these emulsified PI solutions in the preparation of

Table 1. Systematic Screening of a Ternary Parameter Space for the Preparation of PI-Based SEPPI Membranes: Compositions of the Casting Solutions and Performance of the Resulting Membranes in the Separation of RB from IPA (70 μmol L^{-1}, 10 bar, RT)[a]

membrane[b,c]	permeance ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	rejection (%)	OF[d] (−)
PI18/10	4.14 ± 0.12	93.46 ± 0.69	103.52
PI18/14	3.00 ± 0.30	95.18 ± 0.92	88.90
PI18/18	2.90 ± 0.67	95.94 ± 2.01	88.01
PI14/10	6.00 ± 0.51	82.95 ± 4.25	84.57
PI14/14	3.91 ± 0.54	86.37 ± 3.20	84.17
PI14/30	3.66 ± 0.30	86.00 ± 1.24	80.60
PI14/22	4.08 ± 0.33	84.12 ± 6.99	79.57
PI18/22	2.09 ± 0.20	92.70 ± 2.06	71.86
PI22/6	1.20 ± 0.14	98.43 ± 0.30	61.25
PI22/10	0.92 ± 0.16	98.85 ± 0.23	56.67
PI18/30	0.94 ± 0.05	95.17 ± 1.69	55.56
PI18/26	0.74 ± 0.11	96.52 ± 1.15	52.99
PI22/14	0.70 ± 0.08	97.83 ± 0.53	52.79
PI22/18	0.55 ± 0.05	98.60 ± 0.37	50.47
PI22/22	0.49 ± 0.10	98.88 ± 0.58	49.51
PI22/26	0.42 ± 0.07	96.84 ± 0.62	47.83
PI22/30	0.18 ± 0.02	97.24 ± 1.04	43.98
PI14/14	5.79 ± 0.67	70.35 ± 5.60	42.52
Starmem 120	0.81 ± 0.01	99.84 ± 0.01	54.92
MPF-50	0.56 ± 0.09	97.80 ± 0.66	50.46

[a] Membranes sorted according to their OF value. [b] PI*x*/*y* with *x* and *y* representing the PI and NMP-S concentration in the casting solution. [c] THF/NMP weight ratio of 0.33. [d] OF calculated using $R_{\text{threshold}}$ value of 70% and P_{target} value of 6 $L\ m^{-2}\ h^{-1}\ bar^{-1}$.

high-performance SRNF membranes. It is noteworthy however that the applied definition of OF favors highly permeable membranes because chosen target performance was mainly directed toward high fluxes combined with "acceptable" rejections well in the NF domain, rather than very high selectivities.

Quaternary Parameter Space. Subsequently, PI solutions with five different THF/NMP weight ratios varying between 0.33 and 1.25 were systematically studied. A significant influence on membrane performance was anticipated because the cosolvent/solvent ratio is known to be a major tool in adjusting skin layer thicknesses.[3,14] As more solvent can be evaporated from the upper layer of the cast film, increasing THF/NMP ratios will result in a selectivity rise, accompanied with a flux decline. In this quaternary parameter space, a complete systematic screening, involving five different THF/NMP ratios, would obviously be very time-consuming. To illustrate the effect without going through a complete screening, the THF/NMP ratio was only varied for two systems: the casting solution containing 18 wt % PI and 10 wt % NMP-S, resulting in the membrane with the highest OF in the ternary screening (membrane PI18/10), and the polymer solution containing 18 wt % PI and 18 wt % NMP-S, resulting in a more selective but still highly permeable membrane (membrane PI18/18), as shown in Table 2. For the latter system, permeances decrease more sharply with increasing THF content than rejections increase, overall resulting in strongly diminishing OF values. On the other hand, fluxes in the PI18/10 series drop less drastically. While with the applied definition of OF, an optimum is found at a THF/NMP weight ratio of 0.50, membranes with higher THF content would perform better if more importance were given to the selectivity. The cosolvent/solvent weight ratio thus offers an easy tool to direct SEPPI membranes toward a desired performance.

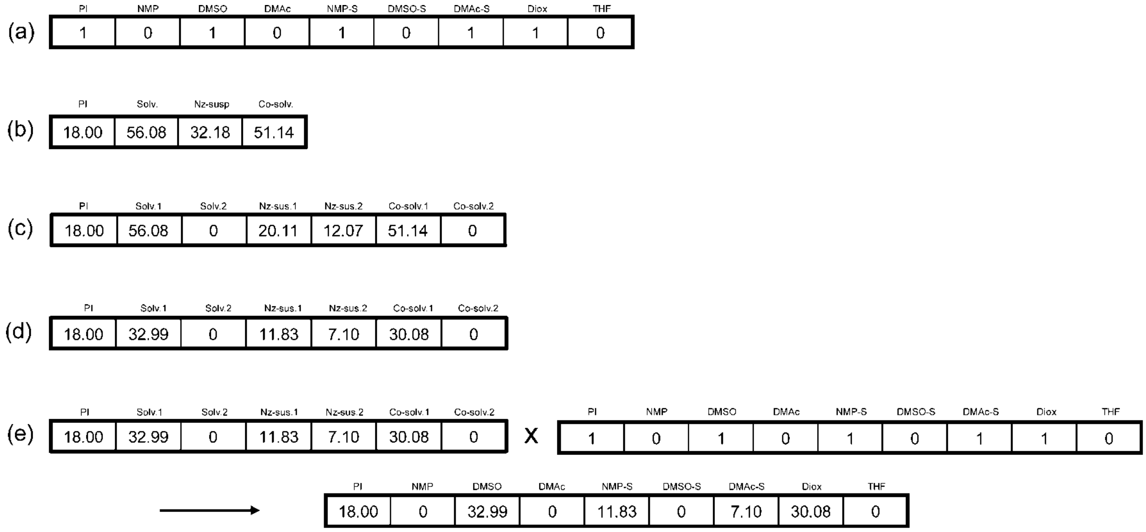
Combinatorial Optimization in a 9-Dimensional Parameter Space. Evolutionary Optimization via Genetic Algorithms. After this preliminary systematic screening, the parameter space was extended with two extra solvents (DMSO and DMAc) and their corresponding nanosized zeolite suspensions (DMSO-S and DMAc-S), as well as another volatile cosolvent (Diox). With optimization of the membrane performance as main goal, this extension of the parameter space was implemented to raise chances on finding the best possible SEPPI membrane. As more constituents allow more complex interactions, which might not be present in a smaller parameter space, the overall optimum is likely to be better, but rather unlikely to be found via a parameter-by-parameter approach. Extra solvents, having different interactions with the coagulant water,[22] organic nanozeolite sols, all containing 8 ± 1 wt % nanosized zeolites and acting as nonsolvent additives,[1] and an extra volatile cosolvent, interfering with the skin layer formation,[3,14] give ample opportunity for fine-tuning. A systematic, "one-at-a-time" screening of this 9-dimensional parameter space would require a tremendous effort. As the combination of a GA and an evolutionary approach[23] already proved to be successful in optimizing the performance of PI membranes in a composition-related parameter space,[20] a similar approach will be applied here to these more complex SEPPI systems. A Visual Basic script was written to set up and guide the optimization process.

First Generation. To create a first generation of casting solutions, 64 one-dimensional 9-digit binary (0/1) arrays, corresponding to the nine selected constituents, were randomly created by an algorithm following a similar procedure as described elsewhere.[19] This is exemplified in Figure 2a for the first composition. In addition to Matrimid, each composition comprised one solvent, one nanosized zeolite suspension, one cosolvent, and an extra component randomly selected from the remaining constituents. This way, three types of compositions were generated, all comprising five components, but containing either a combination of two solvents, a combination of two colloidal zeolite precursor sols, or a combination of two cosolvents. All 64 compositions together form the existence matrix. For each component type, a concentration value was then randomly selected (Figure 2b) from the following concentration ranges set per class of compounds: 14−23 wt% for Matrimid, 30−80 wt% for the solvents, 10−40 wt% for the nanozeolite suspensions and 30−80 wt% for the cosolvents. Subsequently, a one-dimensional matrix with 7 positions was built for each generated composition (Figure 2c). The first position of this matrix was filled with the originally selected PI concentration value, while the remaining 6 positions were divided in three parts, leaving two positions for each type of component. Depending on the composition type, determined by the binary code, these two positions were filled with either the selected concentration value and a zero, or with two new selected concentration values. In the latter case, the following new ranges were applied: 20−100 wt % for the solvents, 1−15 wt % for the nanozeolite sols, and 15−30 wt % for the cosolvents. These two new concentration values were then normalized in such a way that their sum equalled the

Table 2. Influence of the THF/NMP Weight Ratio on the Performance of Two PI-Based SEPPI Membranes in the Separation of RB from IPA (70 μmol L^{-1}, 10 bar, RT)

	PI18/10			PI18/18		
THF/NMP weight ratio	permeance (L m^{-2} h^{-1} bar^{-1})	rejection (%)	OF[a] (−)	permeance (L m^{-2} h^{-1} bar^{-1})	rejection (%)	OF[a] (−)
0.33	4.14	93.46	103.52	2.90	95.94	88.01
0.50	4.10	93.95	103.88	2.86	96.65	87.91
0.75	2.79	95.46	85.82	1.20	96.97	60.79
1.00	2.07	88.93	75.82	0.29	97.69	45.94
1.25	1.19	99.51	61.24	0.00	100.00	41.42

[a] OF calculated using $R_{\text{threshold}}$ value of 70% and P_{target} value of 6 L m^{-2} h^{-1} bar^{-1}.



(a)

PI	NMP	DMSO	DMAc	NMP-S	DMSO-S	DMAc-S	Diox	THF
1	0	1	0	1	0	1	1	0

(b)

PI	Solv.	Nz-susp	Co-solv.
18.00	56.08	32.18	51.14

(c)

PI	Solv.1	Solv.2	Nz-sus.1	Nz-sus.2	Co-solv.1	Co-solv.2
18.00	56.08	0	20.11	12.07	51.14	0

(d)

PI	Solv.1	Solv.2	Nz-sus.1	Nz-sus.2	Co-solv.1	Co-solv.2
18.00	32.99	0	11.83	7.10	30.08	0

(e)

PI	Solv.1	Solv.2	Nz-sus.1	Nz-sus.2	Co-solv.1	Co-solv.2
18.00	32.99	0	11.83	7.10	30.08	0

X

PI	NMP	DMSO	DMAc	NMP-S	DMSO-S	DMAc-S	Diox	THF
1	0	1	0	1	0	1	1	0

→

PI	NMP	DMSO	DMAc	NMP-S	DMSO-S	DMAc-S	Diox	THF
18.00	0	32.99	0	11.83	0	7.10	30.08	0

Figure 2. Generation of casting solution compositions: (a) digitalization of composition and random generation of existence matrix, (b) random generation of concentration values per component type, (c) determination and normalization of concentration values per constituent, (d) overall normalization of the concentration matrix, and (e) generation of actual composition matrix.

generated total concentration of that component type. In a next step, the concentration values of the five components were normalized to 100% (Figure 2d). Because of the relatively small polymer concentration range in which stable SEPPI solutions can be obtained,[1] the PI concentration was kept constant and subtracted from 100%. The concentration values of the other components were normalized to this difference value, and placed in the 7-position matrix, together with the PI concentration values and two zeros. Finally, the actual 64 casting solution compositions were generated by "multiplying" the 64 × 9 digitalized existence matrix with the 7 × 64 concentration matrix (Figure 2e).

The extensiveness of the parameter space and the lack of ternary stability diagrams covering all possible combinations, obviously implies the generation of thermodynamically unstable casting solutions. Of the 64 casting solutions prepared in the first generation, only 40 were useful for membrane synthesis, leaving the 24 others with a zero OF. The instability could generally be ascribed to excessive concentrations of the organic zeolite precursor sols, as well as high cosolvent/solvent ratios or Matrimid concentrations. Because DMSO is a worse solvent for PI than the other two solvents,[24] compositions containing DMSO were often unstable, especially in combination with elevated Matrimid or nanosized zeolite suspension concentrations and with low concentrations of the other two solvents or both. Since all stable polymer solutions were emulsified, the 40 first generation membranes can be regarded as true SEPPI membranes. HT testing of the first generation membranes in the RB/IPA separation generally revealed similar OF values for the top-5 as for the best membranes obtained in the systematic screening. With a peak OF value (OF_{best}) of 94 only, the most promising membranes in the classical screening (Tables 1 and 2) even perform better. The mean OF value (OF_{mean}) of 38 moreover indicates a large diversity between the performances of the first generation membranes.

Second Generation. The second generation, also containing 64 compositions, was generated by applying evolutionary operators, that is, cross-over, quantitative, and qualitative mutation. "Parent" compositions were selected according to the wheel roulette method in a fitness-proportional way, that is, based on their OF values,[15b] and then adapted by cross-over and quantitative mutation to form "offspring" generations. The working principle of these operators on dope compositions is schematically illustrated elsewhere.[19] Cross-over involves the exchange of a series of digits between two composition matrices at a randomly determined exchange position. Quantitative mutation is based on the real concentration values, where one of the values x_i, determined randomly, is changed according to

$$x_i^{\text{new}} = x_i^{\text{old}} + t\frac{x_i^{\text{old}}}{d} \qquad (2)$$

with t being a random integer (−1 or 1) controlling the direction of the concentration change and d determining the step size. These two values were chosen critically per case, based on general phase inversion principles. For qualitative mutation, where a component is added to or eliminated from

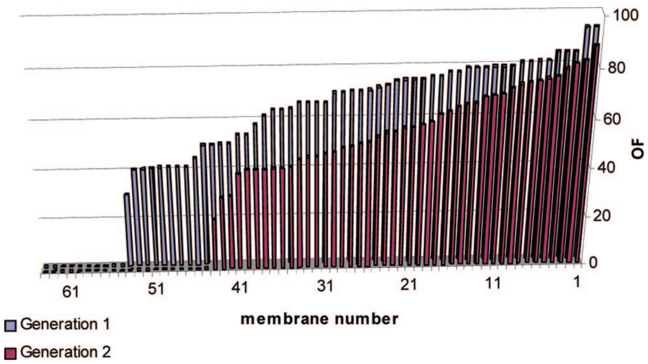


Figure 3. Distribution of the membrane performance over the first and second generations. OF calculated using $R_{\text{threshold}}$ value of 70% and P_{target} value of 6 L m^{-2} h^{-1} bar^{-1}.

a composition, random selection among the entire first generation occurred. After adaptation by one of the operators, the compositions involved were renormalized to 100%.

On the basis of the relationship between OF_{best} and OF_{mean} of the first generation, the application frequencies of the three evolutionary operators in the creation of the second generation were determined by the probabilities W_{cross}, W_{quant}, and W_{qual}. Similar to earlier work,[19,23] these probabilities were defined as

$$W_{\text{cross}} = A\frac{\text{OF}_{\text{best}} - B \times \text{OF}_{\text{mean}}}{\text{OF}_{\text{best}}} \tag{3a}$$

$$W_{\text{qual}} = A\frac{B \times \text{OF}_{\text{mean}}}{\text{OF}_{\text{best}}} \tag{3b}$$

$$W_{\text{quant}} = 1 - A \tag{3c}$$

with the control parameters A and B both fixed at 0.5.

On the basis of the aforementioned OF_{best} and OF_{mean} values of the first generation, W_{cross}, W_{quant}, and W_{qual} values of 0.4, 0.1, and 0.5, respectively, were calculated. Consequently, 18 cross-overs, 4 quantitative, and 23 qualitative mutations were carried out by the GA on the 64 parent compositions. Of the 64 compositions created in the second generation, 45 rendered thermodynamically stable PI solutions from which membranes could be cast, establishing a slight improvement compared to the first generation. The best performing membranes of the second generation generally displayed lower OF values, reflected by a smaller OF_{best} (88) than for the first generation (94). On the other hand, the slightly increased OF_{mean} value (41 versus 38) indicates a lower diversity in the population, with the membranes with weaker performance overall showing a tendency to improve. The observed stagnation of the membrane performance in the second generation (Figure 3) can be explained by the mild selection procedure applied to create this offspring generation. The combination of the relatively low $R_{\text{threshold}}$ value (70%) and the elevated, ambitious P_{target} goal (6 L m^{-2} h^{-1} bar^{-1}) used to calculate OF, was mainly directed toward high permeances, thus allowing poorly performing membranes with high fluxes but relatively low RB rejections (well below 90% being the lower limit of the NF domain) to be selected and subjected to the evolutionary operators. Conversely, this relative lack of selectivity enables a broader screening and thus increases the chances on finding the global optimum in a next generation instead of a local optimum.

Third Generation. To speed up the optimization process and avoid the algorithm "getting lost", a more severe selection was applied on the parent compositions to create the third generation compositions. This was realized by recalculation of the OF values of all membranes of the first and second generations, on the basis of a new P_{target} value of 4 L m^{-2} h^{-1} bar^{-1} and a new $R_{\text{threshold}}$ value of 90%. This way, more selective membranes were rated higher. Better parent compositions would thus be selected, and more performant "offspring" membranes could be anticipated. From all first and second generation membranes, only the best compositions, that is, those resulting in membranes with recalculated OF values exceeding 41 were considered, leaving 39 parent compositions to create the third generation. From these parent compositions, 48 new third generation compositions were created using qualitative and quantitative mutations only. The cross-over operator, which creates more diversity in the population, was not applied to avoid creation of more unstable compositions. With recalculated OF_{best} and OF_{mean} values of 98 and 67, respectively, for the parent population and with the control variables A and B again set at 0.5, W_{quant} and W_{qual} values of 0.24 and 0.76, respectively, were obtained. Hence, 15 quantitative and 33 qualitative mutations were carried out by the GA. Of the 48 prepared PI solutions, 40 membranes could be cast and successfully tested. A significant and general increase of the OF values was noticed, as can be seen in Figure 4, with OF_{best} and OF_{mean} values of 114 and 55, respectively, thus proving the efficiency of the changed selection procedure. The considerable improvement in overall membrane performance, expressed by the increase of the $\text{OF}_{\text{mean}}/\text{OF}_{\text{best}}$ ratio from 0.32 over 0.34 to 0.48 over the three generations, and the concomitant decrease in population variability, reflected by the decreasing ($\text{OF}_{\text{best}} - \text{OF}_{\text{mean}}$) values of 67, 63, and 59, respectively, indicate that the applied GA has progressively been leading to an optimal membrane. A general tendency toward more permeable and selective membranes can be observed in the $R(P)$ diagram shown in Figure 5.

Comparison of Combinatorial Approach with Systematic Screening and Commercial Membranes. The best ten membranes obtained in the combinatorial search were compared with the three best membranes found in the systematic screening and some commercial reference SRNF membranes (Table 3). To allow a correct comparison, the OF values of Tables 1 and 2 were recalculated, using a P_{target} value of 4 L m^{-2} h^{-1} bar^{-1} and a $R_{\text{threshold}}$ value of 90%. The best membranes resulting from the evolutionary optimization show superior OF values to the systematically optimized membranes and generally combine higher IPA permeances with higher RB rejections. Moreover, considering the interactions and the enormous number of combinations in this complex 9-dimensional parameter space, the chance of finding the particular composition of the most performant membrane would have been very small by applying a systematic, parameter-by-parameter approach. It is also remarkable that the top-ten membranes are cast from PI solutions with very diverse compositions, showing totally different combinations of the nine constituents. Despite this diversity, high-

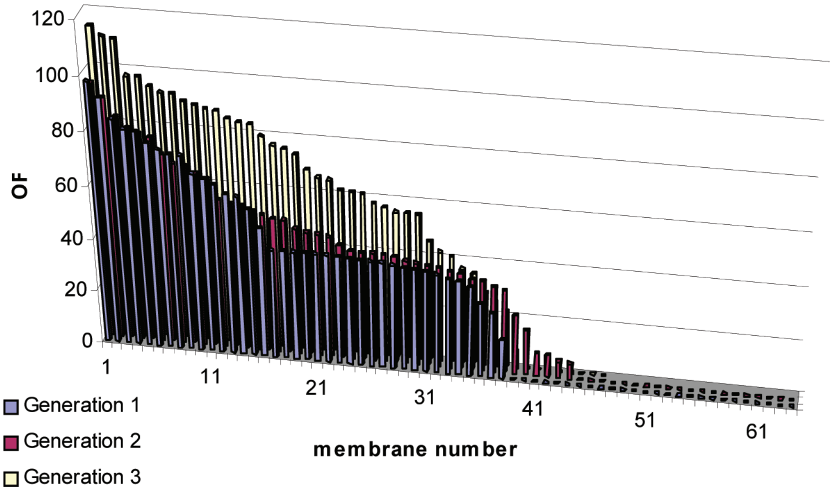


Figure 4. Distribution of the membrane performance over the three generations. OF calculated using $R_{\text{threshold}}$ value of 90% and the P_{target} value of 4 L m^{-2} h^{-1} bar^{-1}.

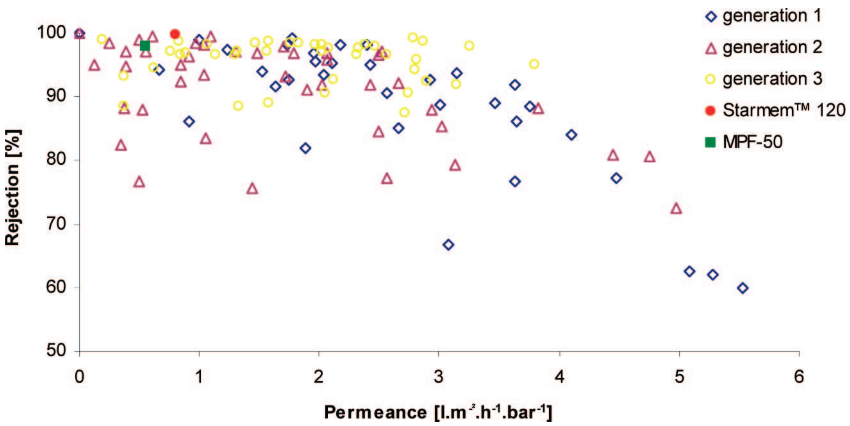


Figure 5. IPA permeances and RB rejections of all membranes prepared in the three generations.

Table 3. Comparison of Combinatorial Optimization, Classical Screening, and Commercial Membranes: Composition of the Casting Solutions and Performance of the Resulting Membranes in the Separation of RB from IPA (70 μmol/L, 10 bar, RT)

no.	PI	NMP	DMSO	DMAc	NMP-S	DMSO-S	DMAc-S	Diox	THF	P (L m^{-2} h^{-1} bar^{-1})	R (%)	OF^{a} (−)
						combinatorial search						
1	20.0		20.37	33.52	9.37			16.75		3.26 ± 0.23	97.98 ± 0.26	114.06
2	19.0	21.72		20.27			9.19		29.82	2.87 ± 0.10	98.77 ± 0.17	110.62
3	19.0	47.46				5.96		12.87	14.71	2.78 ± 0.11	99.23 ± 0.77	109.97
4	19.0			44.23			9.19	12.87	14.71	2.40 ± 0.24	98.26 ± 0.57	97.80
5	20.0	47.19					12.25		20.55	2.46 ± 0.11	97.81 ± 0.54	97.11
6	19.0	41.00			6.46	5.96		12.87	14.71	2.38 ± 0.12	98.19 ± 0.75	97.06
7	19.0	26.81		21.38			12.25		20.55	2.53 ± 0.18	97.23 ± 0.10	95.37
8	19.0			41.17			12.26	12.87	14.71	2.33 ± 0.18	97.72 ± 0.69	93.87
9	19.0	32.63		10.44			11.02		26.90	2.18 ± 0.41	98.17 ± 0.52	92.38
10	18.0	37.82			1.15	8.07		34.95		3.79 ± 0.05	95.09 ± 0.18	92.02
						systematic screening						
1	18.0	42.67		18.00					21.33	2.86 ± 0.03	96.65 ± 0.44	97.44
2	18.0	48.00		18.00					16.00	2.90 ± 0.67	95.94 ± 2.01	92.38
3	18.0	36.00		10.00					36.00	2.07 ± 0.04	98.93 ± 0.04	92.00
						commercial reference membranes						
Starmem 120										0.81 ± 0.01	99.84 ± 0.01	61.65
MPF-50										0.56 ± 0.09	97.80 ± 0.66	52.65

[a] OF calculated using $R_{\text{threshold}}$ value of 90% and P_{target} value of 4 L m^{-2} h^{-1} bar^{-1}.

performance membranes were generally obtained from dopes with Matrimid concentrations between 18 and 20 wt % and relatively low organic zeolite precursor sol concentrations. This holds for both the systematic and the combinatorial approach. Compared with Starmem 120, the optimal membrane shows a 4-fold increased flux, while rejections are only slightly lower. With respect to MPF-50, improvements are even more impressive, with a permeance increase of almost 600% and similar rejections.

Conclusion

The recently demonstrated power of HT experimentation, combined with combinatorial optimization strategies to find compositions of strong-performing membranes, was confirmed here for SEPPI-based SRNF membranes via a direct comparison between a HT/combinatorial approach, a conventional systematic screening, and a selection of commercially available membranes. Asymmetric filled PI membranes were thus prepared from Matrimid solutions rendered emulsified through the addition of an organic nanosized zeolite suspension and were subsequently solidified via immersion−precipitation in water. Membranes were optimized for their SRNF performance, with respect to both permeability and selectivity, in the separation of the dye RB from IPA. Nine parameters, all related to the composition of the casting solutions, were considered, while all other synthesis conditions were kept constant. In first instance, a systematic screening of a restricted quaternary compositional space, comprising PI, NMP, THF, and NMP-S, was carried out. Several promising compositions were thus found leading to highly permeable SEPPI membranes with acceptable RB rejections. After this preliminary screening, a combinatorial optimization study, based on a GA and a self-adaptive evolutionary strategy, was set up in an extended, 9-dimensional parameter space, comprising two extra solvents and the two corresponding zeolite precursor sols, as well as another cosolvent. This directed search led to several high-performance membranes, scoring significantly better with respect to flux and selectivity than the best membranes obtained in the systematic screening, with compositions that would unlikely have been found via ‘traditional” approaches within a reasonable time frame. With IPA permeances up to 3.3 L m^{-2} h^{-1} bar^{-1}, the optimized SEPPI membranes were markedly more permeable than the commercial SRNF membranes Starmem 120 and MPF-50, at similar or slightly lower RB rejections. Coupling of the combinatorial strategy with laboratory-developed HT experimentation techniques enabled the rapid and accurate preparation of 176 casting solutions, and the synthesis and screening of the 125 resulting membranes in less than two months.

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Supporting Information Available. Extensive tables showing the creation of the first, second, and third generation of membranes. This material is available free of charge via the Internet at http://pubs.acs.org.

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